Synthesis and Characterization of Manganese Dioxide Nanoparticles and Thin Films

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DECLARATION

No portion of the work referred to in this dissertation has been submitted in support of an application for another degree of qualification of this or any other university or institution of higher learning.

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ABSTRACT

Stable colloidal suspensions of manganese dioxide were synthesized using different synthesis approaches. The first synthesis approach was by reducing $KMnO_4$ with $Na_2S_2O_3$ in stoichiometric ratio. The second synthesis approach involved redox reaction between stoichiometric amount of reagents $KMnO_4$ and $MnSO_4$ at high pH. The third synthesis approach involved mixing (1:1) molar ratio of the colloidal suspensions prepared by synthesis approach one and two. The manganese concentrations of manganese dioxide colloidal suspensions prepared by first, second and third synthesis approaches were determined by AAS to be 2.65 mg/L, 1.06 mg/L, and 1.45 mg/L respectively. UV-VIS spectra showed two major absorption peaks around 215 nm and 360 nm. These peaks were shifted to higher wavelength and lower energy indicating the formation of larger particles or aggregates upon aging for 30 days. The λ_{max} of dialyzed manganese dioxide colloidal suspension was slightly lower than non-dialyzed manganese dioxide colloidal suspension indicating the relatively smaller particle size. The thin films of manganese dioxide were prepared by drop coating the freshly prepared colloidal suspension directly onto cleaned stainless steel plates. The total manganese dioxide loading of manganese dioxide thin films were 5.03×10^{-3} mg/cm^2, 2.71×10^{-3} mg/cm^2, and 3.48×10^{-3} mg/cm^2 for synthesis approach one, two and three respectively. SEM micrographs showed that the manganese dioxide thin films were generally nanoparticulate and porous in nature. Studies by cyclic voltammetry (CV) showed that the manganese dioxide thin films from both synthesis approaches one and two exhibited good capacitative behaviors in aqueous 0.1M Na_2SO_4 electrolyte.

Key words: Manganese dioxide colloidal suspension, CV, AAS, SEM, UV-Visible

ABSTRAK

Suspensi koloidal mangan dioksida yang stabil disintesis dengan menggunakan kaedah yang berlainan. Kaedah pertama adalah dengan menurunkan $KMnO_4$ dengan $Na_2S_2O_3$ dalam kadar stoisiometrik. Kaedah kedua menggunakan tindak balas redoks antara $KMnO_4$ dan $MnSO_4$ dalam kadar stoisiometrik dan pH yang tinggi. Kaedah ketiga melibatkan campuran (1:1) kadar molar suspensi koloidal daripada kaedah pertama dan kedua. Berdasarkan kajian AAS, kepekatan mangan dalam suspensi koloidal mangan dioksida untuk kaedah pertama, kedua dan ketiga adalah 2.65 mg/L, 1.06 mg/L, dan 1.45 mg/L masing-masing. UV-VIS spektra menunjukkan dua keluk penyerapan pada 215 nm dan 360 nm. Gelombang-gelombang yang beralih ke arah gelombang yang lebih panjang dengan tenaga yang lebih rendah inj menunjukkan pembentukan zarah-zarah yang lebih besar dalam tempoh 30 hari. λ_{max} bagi suspensi koloidal mangan dioksida yang telah didialisis yang lebih rendah daripada suspensi koloidal mangan dioksida yang belum didialisis menunjukkan zarah-zarah yang lebih kecil. Filem nipis mangan dioksida disediakan dengan penyalutan titisan suspensi koloidal secara langsung ke atas kepingan logam tidak berkarat yang bersih. Amaun mangan dioksida dalam filem nipis mangan dioksida adalah 5.03×10^{-3} mg/cm^2, 2.71×10^{-3} mg/cm^2, dan 3.48×10^{-3} mg/cm^2 masing-masing bagi kaedah pertama, kedua dan ketiga. SEM mikrograf menunjukkan filem nipis mangan dioksida adalah zarah-zarah nanosaiz dan berliang-liang kecil. Penentuan dengan menggunakan kitaran voltameter (CV) menunjukkan filem nipis mangan dioksida daripada kedua-dua kaedah mempamerkan kelakuan kapasitatif yang baik dalam larutan akueus elektrolit 0.1M Na_2SO_4.

Kata kunci: Suspensi koloidal mangan dioksida, CV, AAS, SEM, UV-Visible

CHAPTER 1

INTRODUCTION

Over the last decade, there has been increased interest in 'nanotechnology'. The nanotechnology is defined as the science and engineering of making materials, functional structures and devices on the order of a nanometer scale (Nalwa, 2000). Based on the nanotechnology, most of recent studies have focused on the synthesis of the nanostructure materials. The nanostructures are particles, grains, functional structures and devices with dimensions in the 1–100 nanometer range (Nalwa, 2000). In the recent years, Feldheim and Foss (2002) have reported that there are three emerging themes in nanoparticles researches in the current literatures. The first is the synthesis and assembly of nanoparticles of well-defined size and geometry. Secondly, the structural and surface chemistry effects on single electron changing and lastly the size, shape and surface chemistry effects on particle optical properties.

One of the most interested nanoparticles is the manganese oxide due to its useful applications especially in the electronic devices. Manganese is a grey white metal with an atomic radius about 140 pm. It is a hard metal and is very brittle, fusible with difficulty but easily oxidized. Manganese oxide compounds can be used as an external catalyst, lithium batteries, paints, coloured glass, fertilizers, textile printing, ceramics, and as food additives. Due to their low cost, environmental merit and easy preparation, many researches have been conducted to synthesize nanostructured manganese oxides (Mavchefaux *et al*., 2006).

Manganese oxide in its nanoparticle size form is being widely used in the lithium-ion batteries. Nevertheless, the utilization of manganese oxide in the batteries has been plaqued by problems of moderate capacity and poor stability (Liu *et al*., 2006). A research has been carried out to synthesis nanostructured manganese oxide that exhibits outstanding cycling stability and with high discharge capacity. Liu *et al.* (2006) has reported an electrodeposition process in the presence of a non-ionic surfactant such as Brij^{TM} 56 ($C_{16}H_{33}(OCH_2CH_2)_8H$).

On the other hand, various methods have been developed to produce stable manganese oxide thin-film electrode for its application as supercapacitors. Supercapacitors have the unique characteristic of high power density, excellent reversibility and longer cyclic life in comparison with batteries (Huang *et al*., 2006). Several recent methods that have been reported for the synthesis of manganese oxide thin film electrodes included electrostatic spray deposition (Dai *et al.*, 2006) and anodic deposition method (Huang *et al.,* 2006). In addition, hydrothermal synthesis of nanostructured MnO_2 could further improve the capacitance and cycling efficiency of the manganese dioxide, MnO_2 electrochemical system. This was due to the fine tunings of pore structures and structural morphologies (Subramanian *et al*., 2006).

Furthermore, synthesis of metal oxides by the sol-gel method is one is the popular methods recently. It is widely used due to its various advantages. The advantages of sol-gel method included that almost any metal oxide system can be examined and no special apparatus or equipment is required. It works well for the synthesis of complex metal oxides with high phase purity. This is because it consists of polymerizing gel which traps the various metal ion

components spatially, permitting precipitation from solution where all the metal ions occupy near-neighbor positions in the gel matrix (Moser *et al*., 2001).

Besides, sol-gel processing also exhibits good control over microstructure and particle morphology in the synthesis, typically at room temperature (Moser *et al*., 2001). According to Hwang *et al.* (2006) paper, the sol-gel method has advantages such as good control of stoichiometry, lower calcinations temperature, relatively shorter processing time and production of micron sized particles with narrow particle size distribution. Thus, this method is highly preferable if compared to the solid-state method which is not possible to control particle size because it involves high temperature, long and repeated heat treatments and extended grinding.

Furthermore, many researches on modifying and improving the structure of the manganese oxide have been done to extend the use of manganese oxide in various applications such as super capacitor and secondary batteries. Super capacitor has the potential applications in loading leveling functions for batteries in electric vehicles during starting, acceleration and regenerative braking and burst power generation in electronic devices such as cellular phones, camcorders and navigational devices (Huang *et al*., 2006).

In this study, stable manganese oxide colloidal suspension with different particle size will be synthesized by using various synthesis approaches. The physical and chemical properties of these manganese oxide colloidal suspensions will be characterized by using different instruments such as scanning electron microscopy (SEM), scanning UV-VIS spectrophotometer, atomic

absorption spectroscopy (AAS), and cyclic voltammetry. Beside that, effect of dialysis process in the synthesis will be investigated, too.

Among the objectives of this study include:

a) To prepare stable manganese oxide colloidal suspensions by various different synthesis approaches.
b) To characterize the physical and chemical properties of these colloidal suspensions of manganese oxide.
c) To optimize synthesis conditions for effective particle size control of manganese oxide nanoparticles.

CHAPTER 2

LITERATURE REVIEW

Various methods have been developed for the synthesis of nanostructured manganese oxide in the recent time. However, the stable nanoparticles of manganese oxide can be difficult to prepare due to its strong tendency to precipitate or coagulate during synthesis. Brock *et al.* (1999) reported the successful preparation of stable colloids of lamellar manganese oxide from reduction of tetraalkylammonium (tetramethylammonium, tetraethylammonium, tetrapropylammonium, and tetrabutylammonium) permanganate precursors. Besides, the preparation of microporous manganese oxides by nonaqueous sol-gel reactions involving tetrabutylammonium (TBA) or tetraethylammonium (TEA) permanganate and methanol in the presence of alkali cation dopants have been reported (Ching *et al*., 2002). In the latest research by Ching *et al.* (2004), the quality of manganese oxide thin films with higher selectivity by the layered birnessite structure obtained from nonaqueous sol-gel processing is compared to analogous preparation of aqueous gels. This can be proven by the superior surface wetting property afforded by nonaqueous sols, which promotes a more uniform coating. Another factor that improved the quality of thin films is the gelation time.

According to Ching *et al*. (2004), spin coating with nonaqueous sol-gel mixtures provides an excellent route to produce high quality manganese oxide thin films in terms of crystallinity, smoothness and uniform thickness. Ching *et al*. (2004) used Chemat KW-4B spin coater in spin coating manganese oxide sols onto approximately 2.5 cm x 2.5 cm substrates that included soft

glass, quartz glass and Ni foil substrates. Birnessite-type manganese oxides were obtained on soft glass using sol-gel films with alkali metal cations added as dopants (Li^+, Na^+ ,K^+, Rb^+, or Cs^+). In the absence of these alkali dopants, thin films of nonporous Mn_2O_3 would be obtained. Ching *et al.* (2002) stated that non-aqueous sol-gel routes would produce microporous manganese oxides with birnessite, cryptomelane and spinel structures. Thus, alkali-metal cations play a key role as dopants or templates for the microporous frameworks.

The synthesis of lithium manganese spinels have been widely studied due to its large reverse capacity, low cost and low toxicity (Hwang *et al*., 2001; Kopeć *et al*., 2006; Molenda *et al*., 2005; Park *et al*., 2006). Methods that were developed recently for the syntheses of lithium manganese spinels include the sol-gel method (Hwang *et al*., 2001) and ultrasonic spray pyrolysis (Park *et al*., 2006).

The synthesis of lithium manganese spinels $LiMn_2O_4$ by the sol-gel method is using citric acid as a chelating agent was reported by Hwang *et al.* (2001). The solution pH was adjusted to 7.0 with ammonium hydroxide, NH_4OH and the entire process was carried out under continuous stirring. Then, calcination was done at various temperatures such as 300, 400, 500, 600, 700 and 800^oC in air. In ultrasonic spray pyrolysis, its starting solution pH was also maintained at 7.0 with NH_4OH. The calcination of manganese oxide powders were done at 500^oC and 800^oC. To synthesize $LiMn_2O_4$ powders using ultrasonic spray pyrolysis, the starting materials used were $LiNO_3$ (Aldrich) and $Mn(NO_3)_2.4H_2O$ (Sigma) (Park *et al.*, 2006).

Both methods above concluded that increased in the calcination temperatures will increased the crystallinity of the lithium manganese spinel, $LiMn_2O_4$. Park *et al.* (2006) reported that the $LiMn_2O_4$ powders synthesized at high calcination temperature were no longer nano-sized due to crystal growth of the nano-sized particles by high temperature calcination. Their sizes ranged from 100 to 300 nm. Thus, these methods are considered to be promising alternative synthesis routes for nanocrystalline materials suitable for lithium secondary batteries.

The cathode material plays an important role in the performance of lithium ion batteries. The $LiMn_2O_4$ spinel material in commercial lithium batteries showed capacity fading during prolonged cycling, decreased in the initial capacity and low rate capability (Hwang *et al.*, 2002). According to Zheng *et al.* (1997), spinel doped with single metal ions offers higher capacity as compared to the practical capacity obtained from the undoped spinel cathode. Hwang *et al*., (2002) reported that a multidoped spinel phase of $Li_{1.02}Co_{0.1}Ni_{0.1}Mn_{1.8}O_4$ which was synthesized by the sol-gel process delivered high initial capacity and showed excellent stability at both low and high C-rates.

Based on solid-state method developed by Na *et al.* (2006), the doped spinel $LiCo_{0.02}La_{0.01}Mn_{1.97}O_{3.98}Cl_{0.02}$ powder had similar morphology and particle size distribution with undoped $LiMn_2O_4$, but larger particle size and lower specific area. Besides, coatings obtained by electrophoretic deposition method were highly uniform, exhibited good adherence to the substrate and also their thickness could be easily controlled (Caballero *et al*., 2006).

Furthermore, Wang and Cao (2006) also investigated the Li^+-intercalation electrochemical or electrochromic properties of vanadium pentoxide films by sol electrophoretic deposition. In their paper, thin films of orthorhombic V_2O_5 have been prepared by sol electrophoretic deposition (EPD). Wang and Cao (2006) have mentioned that the nanostructured V_2O_5 electrode that made from electrophoretic deposition has higher rate capabilities and is promising for use in compact batteries. In addition, V_2O_5 films prepared from sol electrophoretic deposition also promise higher porosity and better Li^+-intercalation performance.

The current density and film thickness have been reported to have considerable effect on the morphology of the porous surface layer of manganese oxide (Djurfors *et al*., 2006). A higher current density resulted in a much thinner, finer porous layer whereas thicker deposited Mn films gave much thicker porous films. The increased in the current density would give greater hydration and capacitance. In the other words, the porous film was the key to developing the high capacitance as shown by these films (Djurfors *et al*., 2006).

The characterization of these films could be done by various types of established methods such as powder X-ray diffraction spectroscopy (XRD), scanning electron microscopy (SEM), galvanostatic charge/discharge test (Liu *et al*., 2006), atomic absorption spectroscopy (AAS), X-ray photoelectron spectroscopy (XPS) using a Kratos AXIS 165 X-ray Photoelctron Spectrometer (Djurfors *et al*., 2006) and Scanning UV-VIS spectrophotometer or optical spectra (Wang and Cao, 2006).

Djurfors *et al*. (2006) reported the use of X-ray photoelectron spectroscopy (XPS) to examine both valence of manganese in the porous film and the relative hydration of these films. They reported that the highest current density resulted in incomplete oxidation and a two-phase mix of manganese dioxide, MnO_2 with trace amount of Mn_2O_3. Thus, the higher current density would result in rapid imposed oxidation rate to completely oxidize the porous layer prior to the potential of 0.9V. Djurfors *et al*. (2006) concluded that the film hydration increased with increasing of current density and contributed positive effect on capacitance. Besides, Djurfors *et al*. (2006) also examined the relationship between the oxidizing current density and capacitance with cyclic voltammetry. The current densities of 0.2, 0.4, 0.8 and 1 mA cm^{-2} were used to evaluate their effect on capacitance.

For characterization of manganese oxide thin films, Ching *et al.* (2004) used powder X-ray diffraction (XRD) to measure the spacing patterns of birnessite thin films. Powder X-ray diffraction (XRD) measurements were performed with CuKα radiation. The samples were scanned at 5° 2θ/min. The beam voltage and beam current were 30 kV and 15 mA, respectively. Machefaux *et al*. (2006) used a Siemens D5000 Bragg-Brentano (θ–2θ configuration) diffractometer for the 2θ range 10-75° in his study of characterization of hollandite (α), pyrolusite (β) and γ structures phase and phase mixtures.

Besides, the morphologies of manganese oxides could be examined by scanning electron microscopy (SEM) (Liu *et al*., 2006 and Huang *et al*., 2006). Huang *et al*. (2006) observed the surface morphology of manganese oxide electrodes using a scanning electron microscope (SEM) (Hitachi-650). They examined the surface morphology of the manganese oxides that deposited at

various potentials. Then, they reported that the surface morphology of the manganese oxides changed with the change of potential. The size of manganese oxide particles deposited became larger and the thickness of manganese oxide films turned thicker at higher potential.

Dai *et al*. (2006) studied the surface morphology of manganese oxide using a scanning electron microscope (Hitachi S-4700). They reported that the structure of manganese oxide thin films prepared by electrostatic spray deposition (ESD) were rough and porous with many cracks. The cracked surfaces were related to large volume change occurred during the drying process. Thus, Dai *et al*. (2006) reported that the specific capacitance (SC) was significantly affected by the surface morphology of the electrode material because the electrolyte was facile to penetrate into the porous and cracked manganese oxide film.

CHAPTER 3

METHODOLOGY

3.1 Preparation of Manganese Dioxide Colloidal Suspension

In this study, colloidal suspensions of manganese dioxide were prepared using three different synthesis methods as reported by Perez-Benito *et al.* (1996), Sostaric *et al.* (1995) and mixture of colloidal suspension prepared by both methods.

(a) Synthesis Approach 1:

The first synthesis method for preparing manganese dioxide colloidal suspension was based on method reported by Perez-Benito *et al.* (1996). The colloidal suspension was prepared by mixing 2.5 mL of $KMnO_4$ (1.00×10^{-1} mol dm^{-3}) and 5 mL of $Na_2S_2O_3$ (1.88×10^{-2} mol dm^{-3}) aqueous solutions in a 500 mL volumetric flask. Ultrapure water was then added until completion. The solution was being homogenized by gentle stirring for about two hours to mix the solution well. The resulting solution was transferred into 3500MW dialysis tubes and dialyzed against 7L ultrapure water for 4 days. The water was changed after 1, 4, 16, 72 hours. The pH was tested during each water changing process to monitor and avoid considerable pH change. The synthesis protocol of manganese dioxide colloidal suspension is briefly illustrated in Figure 3.1.

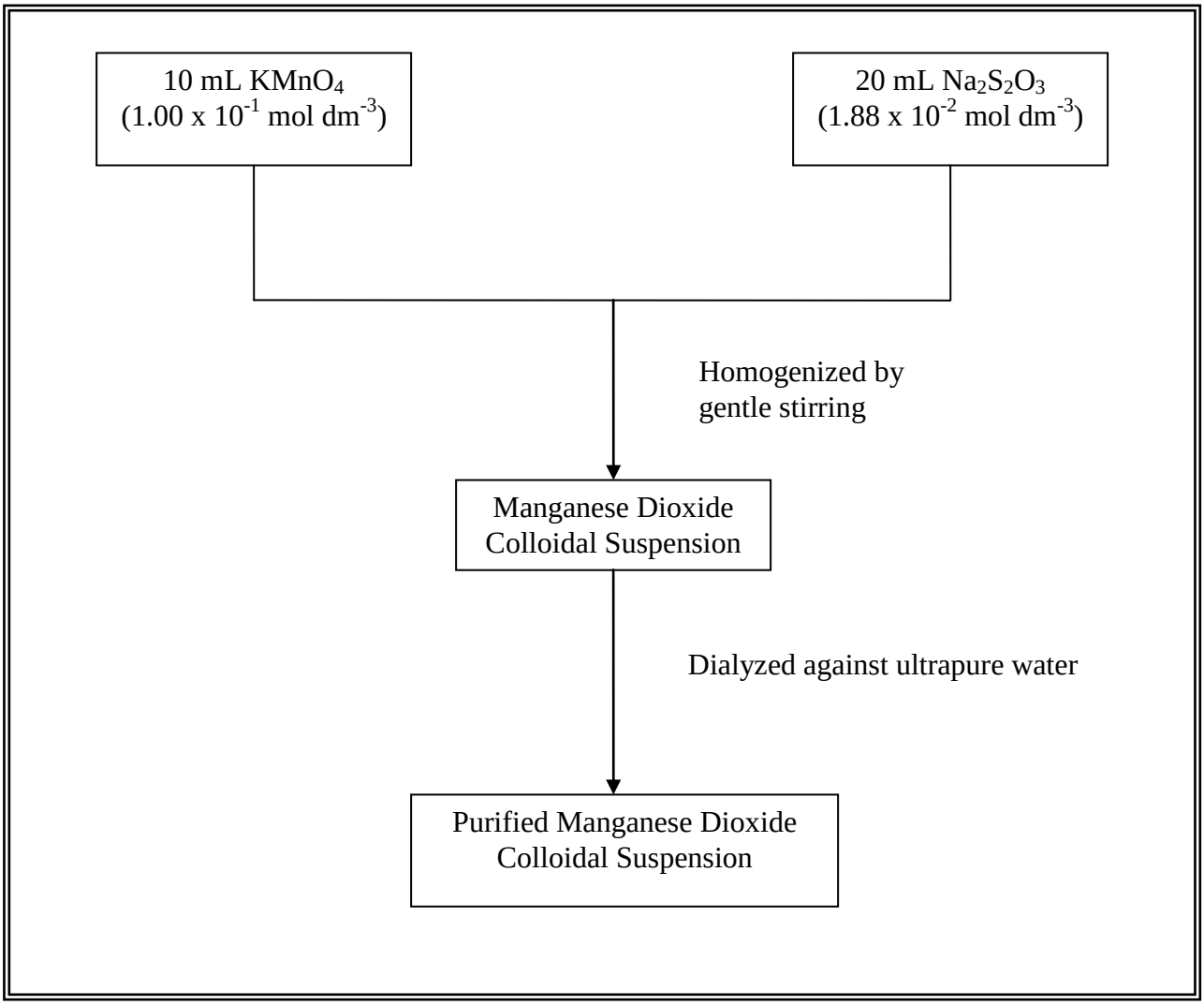

Figure 3.1: Preparation of manganese dioxide colloidal suspension based on method reported by Perez-Benito *et al.* (1996).

(b) Synthesis Approach 2:

The second method for preparing manganese dioxide colloidal suspension was based on method reported by Sostaric *et al.* (1995). $KMnO_4$ was added to NaOH to produce a 500 mL

solution of 8.00 x 10^{-5} mol dm^{-3} MnO_4^- at pH 10.5 ± 0.2. After that, 7.50 x 10^{-3} mol dm^{-3} $MnSO_4$ (0.8 mL) was rapidly added by micropipette to the vigorously stirred permanganate solution. The resulting colloidal suspension was being placed into dialysis tubes, 3500 MW, and dialyzed against 7L ultrapure water. The ultrapure water was changed after 1, 4, 16, 72 hours and dialyzed for a total of 93 hours. The procedure for preparing manganese dioxide colloidal suspension above is briefly illustrated in Figure 3.2.

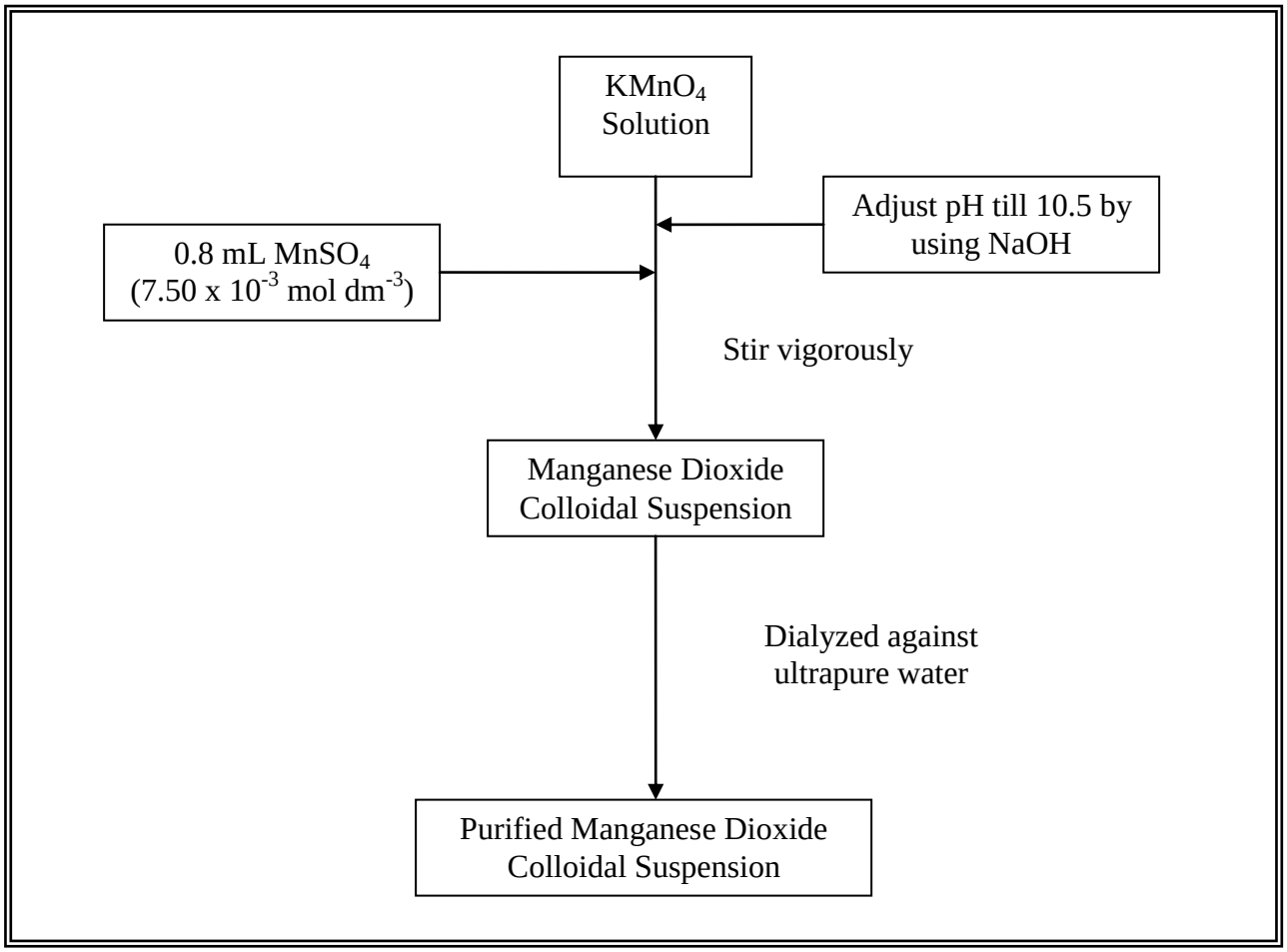

Figure 3.2: Preparation of manganese dioxide colloidal suspension based on method reported by Sostaric *et al.* (1995).

(c) Synthesis Approach 3:

The third approach for preparing manganese dioxide colloidal suspension was done by mixing up both manganese dioxide colloidal suspension that prepared by synthesis approach one and synthesis approach two in term of molar ratio 1:1. 30 mL of 5.00 x 10^{-4} mol dm^{-3} manganese dioxide colloidal suspension from first synthesis method was taken out and pour into a beaker containing 75 mL of 2.00 x 10^{-4} mol dm^{-3} manganese dioxide colloidal suspension from second synthesis method. The mixture was then stirred for two hour to mix the colloidal suspension thoroughly. The procedure for preparing manganese oxide colloidal suspension above is briefly illustrated in Figure 3.3.

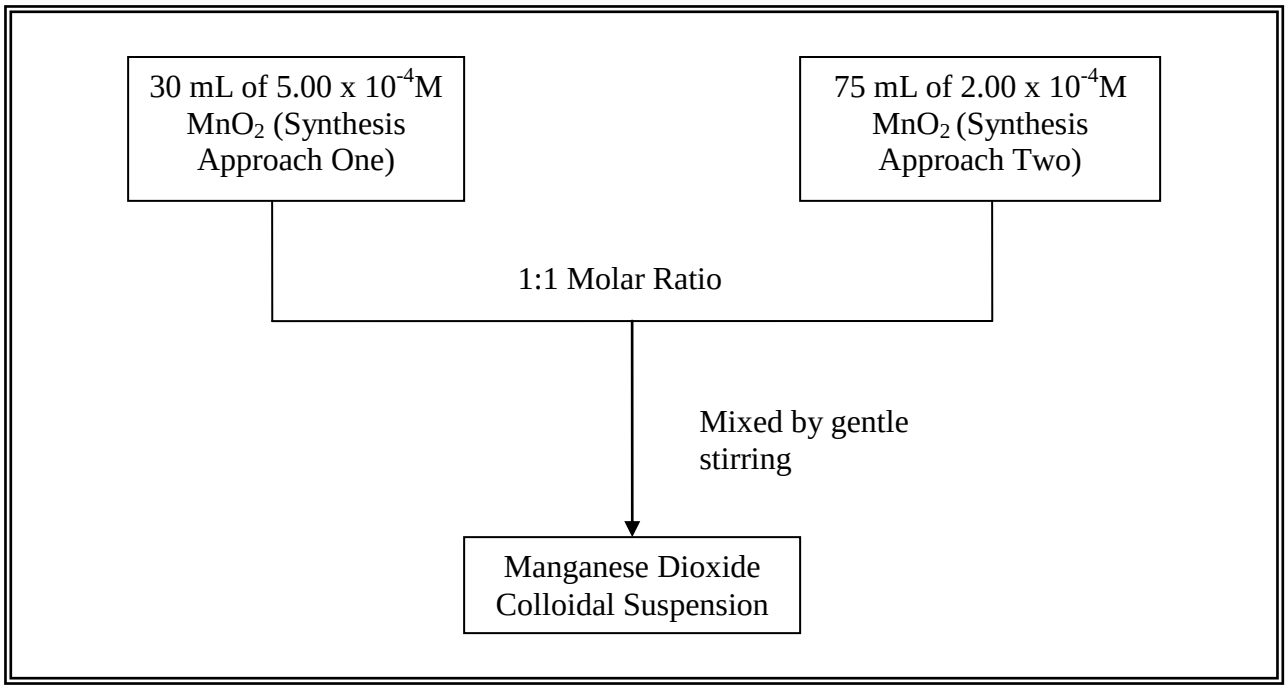

Figure 3.3: Preparation of manganese dioxide colloidal suspension with synthesis approach one and synthesis approach two.

3.2 Preparation of Manganese Dioxide Thin Films

About 100 pieces of stainless steel plates (4 cm x 1.5 cm) were being prepared. Every stainless steel plate was being polished using sand paper no. 1000 to remove the oxidized surface layer and then being cleaned with detergent. The stainless steel plates were placed in a beaker containing detergent solution and sonicated for 15 minutes. They subsequently cleaned by sonicating in ultrapure water for another 15 minutes. This step was followed by sonicating with HNO_3 acid and acetone. Sonicating with ultrapure water has to be carried out in between these steps and each sequence took 15 minutes. Finally, the stainless steel plates were being dried in oven at 105 ^{o}C. All of the stainless steel plates were individually labeled and weighed. All these cleaning steps were deemed necessary in order to obtain clean stainless steel plates so that pure and uniform coating would be formed on them and the charge capacity of these coatings would not be affected.

The manganese dioxide colloidal suspensions were being well dispersed by sonication. Manganese dioxide thin films were prepared by drop coating onto precleaned stainless steel plates. 0.3 mL of sonicated manganese dioxide colloidal suspension was dropped onto 1.5 x 1.5 cm stainless steel plates to produce manganese dioxide thin films and then was allowed to dry in the desiccators. Each type of thin films was done in triplicates to obtain average results.

3.3 Characterization of Manganese Dioxide Nanoparticles and Thin Films

The characterization of the manganese oxide colloidal suspension and thin films were done by Scanning UV-VIS Spectrophotometer, Atomic Absorption Spectrophotometer (AAS), Scanning Electron Microscope (SEM), and Advanced Electrochemical Analyzer. The physical and electrochemical properties of manganese dioxide nanoparticles and thin films samples were determined by using these characterization techniques.

3.3.1 Atomic Absorption Spectrophotometer (AAS)

The concentration of manganese oxide colloidal suspensions and the mass of thin films was determined by Flame Atomic Absorption Spectrophotometer (AAS) Perkin-Elmer model 3110.

10 mL of freshly prepared manganese dioxide colloidal suspension was digested with 3 mL of 10% nitric acid (HNO_3) and 3 mL of 10% peroxide acid (H_2O_2). The resulting solution was diluted to 100 mL with ultrapure water. Similarly, freshly coated manganese dioxide thin films were digested with 3 mL of 10% nitric acid (HNO_3) and 3 mL of 10% peroxide acid (H_2O_2) and then diluted to 100 mL with ultrapure water. Each type of samples was being analyzed in triplicates to determine the average concentration of manganese and hence the concentration of manganese dioxide in the colloidal suspension as well as the mass of manganese dioxide in the